FINAL TECHNICAL REPORT

Project Number: **88563**
DE-FG07-02ER63489

Project Title: Phosphate Barriers for Immobilization of Uranium Plumes

Co-Principal Investigator: Peter C. Burns, Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, IN 46556, (574) 631-5380, pburns@nd.edu

Number of Graduate Students Involved: 2

Number of Undergraduate Students Involved: 2

RESEARCH OBJECTIVES

Uranium contamination of the subsurface has remained a persistent problem plaguing remedial design at sites across the U.S. that were involved with production, handling, storage, milling, and reprocessing of uranium for both civilian and defense related purposes. Remediation efforts to date have relied upon excavation, pump-and-treat, or passive remediation barriers (PRB's) to remove or attenuate uranium mobility. Documented cases convincingly demonstrate that excavation and pump-and-treat methods are ineffective for a number of highly contaminated sites. There is growing concern that use of conventional PRB's, such as zero-valent iron, may be a temporary solution to a problem that will persist for thousands of years. Alternatives to the standard treatment methods are therefore warranted. The core objective of our research is to demonstrate that a phosphorous amendment strategy will result in a reduction of dissolved uranium to below the proposed drinking water standard. Our hypothesis is that long-chain polyphosphate compounds forestall precipitation of sparingly soluble uranyl phosphate compounds, which is key to preventing fouling of wells at the point of injection.

RESEARCH ACCOMPLISHMENTS AND IMPLICATIONS

This report summarizes work conducted at the University of Notre Dame under DOE grant DE-FG07-02ER63489, which has been funded since September, 2002. The objectives at Notre Dame are development of synthesis techniques for uranyl phosphate phases, together with detailed structural and chemical characterization of the myriad of uranyl phosphate phases that may form under geochemical conditions under consideration. It is important to note that the state of knowledge concerning uranyl phosphates at the outset of this project was very poor. These were a poorly characterized group of compounds with uncertain structures and unknown water contents. Our research has greatly impacted understanding of the structures and chemistries of uranyl phosphates and arsenates. Fifteen papers reporting the findings of our studies concerning the synthesis, structures and compositions of these compounds have been published (see below). This grant funded Andrew Locock's doctoral dissertation research "Crystal chemistry of uranyl phosphates, arsenates, and oxysalts of chromium(V): Implications for remediation".

Synthesis techniques were developed that provide excellent single crystals of a variety of uranyl phosphates, including the very important autunite and meta-autunite groups. Most techniques involve diffusion of nutrients in silicon-based gels at room temperature. Other novel techniques are based upon mild hydrothermal reactions. Details of the synthesis techniques are provided in the 15 published papers.

Complete crystal structure determinations have been accomplished using single-crystal X-ray diffraction data collected using a CCD-based detector. Fifteen papers have been published that report the details of these synthesis techniques and the crystal structures of the target phases. Most of these papers focus on the autunite or meta-autunite group phases, as these are the most likely to form in the subsurface where phosphate is added to groundwater as a remediation strategy. Included in these studies is the first reported full structure of autunite, as well as that of triuranyl diphosphate tetrahedrate. New framework structural topologies were also discovered that contain sheets based upon the uranophane anion topology.

Our research on the detailed structures and compositions of uranyl phosphates and arsenates is the basis on which to build a sophisticated understanding of the stabilities of these minerals under environmental conditions. We have synthesized several uranyl phosphates of the autunite group and studied their thermochemistry. Our emphasis has been on deriving an internally consistent thermochemical dataset for these uranyl phosphate compounds. The enthalpies of formation of nine uranyl phosphates have been determined using high-temperature oxide melt solution calorimetry. All materials studied were synthetically prepared and characterized by X-ray powder diffraction, Energy Dispersive Spectroscopy, and Thermal Gravimetric Analysis. Data has been collected for: metatorbernite, $Cu(UO_2)_2(PO_4)_2(H_2O)_{8;}$ meta-autunite, $Ca[(UO_2)(PO_4)]_2(H_2O)_6$; the Sr analogue of meta-autunite, $Sr[(UO_2)(PO_4)]_2(H_2O)_6$; meta-ankoleite, $K(UO_2)(PO_4)(H_2O)_3$; the Rb analogue of meta-ankoleite, $Rb(UO_2)(PO_4)(H_2O)_3$; the Tl analogue of meta-ankoleite, $Tl(UO_2)(PO_4)(H_2O)_3$; the Ag analogue of meta-ankoleite, $Ag(UO_2)(PO_4)(H_2O)_3$; uramphite, $NH_4(UO_2)(PO_4)(H_2O)_3$ and $(UO_2)_3(PO_4)_2(H_2O)_4$.The enthalpy of formation from the binary oxides, $\Delta H_{f\text{-ox}}$, at 298 K was calculated for each compound from the respective drop solution enthalpy, ΔH_{ds}. The obtained values are useful in exploring the stability of uranyl phosphates in chemical systems of environmental importance, such as those expected in U-contaminated environments. A manuscript reporting these measurements has been drafted, and will be submitted for publication shortly.

INFORMATION ACCESS

1. Locock, A.J., Kinman, W.S. & Burns, P.C. (2005): The structure and composition of uranospathite, $Al_{1-x}\square_x[(UO_2)(PO_4)]_2(H_2O)_{20+3x}F_{1-3x}$, x = 0 – 0.33, a non-centrosymmetric fluorine-bearing mineral of the autunite group, and a related synthetic lower hydrate, $Al_{0.67}\square_{0.33}[(UO_2)(PO_4)]_2(H_2O)_{15.5}$. *Canadian Mineralogist* 43, 989-1004.

2. Locock, A.J. & Burns, P.C. (2005): Structures of strontium and barium-dominant compounds that contain the autunite-type sheet. *Canadian Mineralogist* 43, 721-733.

3. Locock, A.J., Burns, P.C. & Flynn, T.M. (2005): The role of water in the structures of synthetic hallimondite, $Pb_2[(UO_2)(AsO_4)_2](H_2O)_n$ and synthetic parsonsite, $Pb_2[(UO_2)(PO_4)_2](H_2O)_n$, $n \leq 0.5$. *American Mineralogist* 90, 240-246.

4. Locock, A.J., Burns, P.C., Duke, M.J.M. & Flynn, T.M. (2004): Monovalent cations in structures of the meta-autunite group. *Canadian Mineralogist* 42, 973-996.

5. Locock, A.J. & Burns, P.C. (2004): Structures and synthesis of layered and framework amine-bearing uranyl arsenates and phosphates. *Journal of Solid State Chemistry* 177, 2675-2684.

6. Locock, A.J. & Burns, P.C. (2004): Revised Tl(I)-O bond valence parameters and the structures of thallous dichromate and thallous uranyl phosphate hydrate. *Zeitschrift fur Kristallographie* 219, 1-8.

7. Burns, P.C., Alexopoulos, C.M., Hotchkiss, P.J., Locock, A.J. (2004): An unprecedented uranyl phosphate framework in the structure of $[(UO_2)_3(PO_4)O(OH)(H_2O)_2](H_2O)$. *Inorganic Chemistry* 43, 1816-1818.

8. Locock, A.L. & Burns, P.C. (2003): The structure of hügelite, an arsenate of the phosphuranylite group, and its relationship to dumontite. *Mineralogical Magazine* 67, 1109-1120.

9. Locock, A.J. & Burns, P.C. (2003): Structures and synthesis of framework triuranyl diarsenate hydrates. *Journal of Solid State Chemistry* 176, 18-26.

10. Locock, A.L. & Burns, P.C. (2003): Structures and synthesis of framework Rb and Cs uranyl arsenates and their relationships with their phosphate analogues. *Journal of Solid State Chemistry* 175, 372-379.

11. Locock, A.J. & Burns, P.C. (2003): Crystal structures and synthesis of the copper members of the autunite and meta-autunite groups: torbernite, zeunerite, metatorbernite and meta zeunerite. *Canadian Mineralogist* 41, 489-502.

12. Locock, A.J. & Burns, P.C. (2003): The crystal structure of bergenite, a new geometrical isomer of the phosphuranylite group. *Canadian Mineralogist* 41, 91-101.

13. Locock, A.L. & Burns, P.C. (2003): The crystal structure of synthetic autunite, $Ca[(UO_2)(PO_4)]_2(H_2O)_{11}$. *American Mineralogist* 88, 240-244.

14. Locock, A.L. & Burns, P.C. (2002): Crystal structures of three framework alkali metal uranyl phosphate hydrates. *Journal of Solid State Chemistry* 167, 226-236.

15. Locock, A.J. & Burns, P.C. (2002): The crystal structure of triuranyl diphosphate tetrahydrate. *Journal of Solid State Chemistry* 163, 275-280.